

In-situ Synchrotron WAXD/SAXS Studies of Structural Development during PBO/PPA Solution Spinning

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Beamline(s): X27C

Introduction: Polybenzoxazole (PBO) is one of the high performance fibers, which has a semi rigid rod molecular structure. The general method for the manufacture of PBO fiber starts with a dry-jet wet-spinning process from a solution of the polymer ^[1]. The properties of spun fibers are highly dependent on the spinning conditions. These processing conditions control the structure and morphology of the spun fiber. Thus it is very interesting to study the structure and morphology changes dynamically during spinning processing and the coagulation process.

Methods and Materials: Spinning experiment was carried out at X27C SUNY beam line at NSLS/BNL. The x-ray beam ($\lambda = 0.137$ nm) passes through 3-pinhole system (190 cm long) with the first and last pinhole size of 0.10 mm and 0.37 mm in diameter, respectively. The spin unit is a modified version of the experimental unit used by The DOW Chemical Company ^[2]. Using a custom-designed X-ray beam spot monitoring system, the synchrotron beam was easily aligned with the fiber having a diameter of about 50 μm . Monofilament fiber from the spinneret was exposed to the X-ray beam for about 2 min. Separate two-dimensional (2D) WAXD and SAXS patterns were recorded by using a CCD X-ray detector (MAR-USA). The distance between the detector and the sample for WAXD was 112.9 mm. For SAXS, the distance between the detector and the sample was 1437.5 mm.

Results: WAXD patterns (shown in Fig.1) indicate that the structure before coagulation has a lyotropic liquid-crystalline order that cannot be simple nematic phase or disordered crystal phase. The best model to describe this intermediate structure is a biaxial nematic phase based on plank-shaped structural unit with PBO-PPA complex. A different type of biaxial nematic phase with PBO chains as mesogenic units develops upon coagulation in water even in a very short period of time (~ 2 seconds). When the coagulation time increases (30 min), the PBO-PPA complex structure disappears completely and pure PBO crystals are fully formed. The meridian peaks showed streaks and no obvious off-axis reflections, indicating these crystals had translational disorder. 2D SAXS patterns of the PBO fiber after coagulation showed equatorial streaks, probably due to the microvoid structure.

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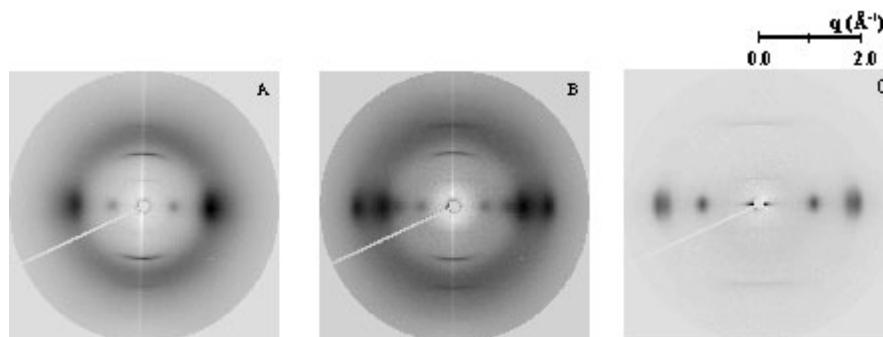


Fig.1. 2D WAXD patterns of PBO fiber with SDR of 10.0, bath temperature of 60 °C at different stages: A) before coagulation, B) 2 s of coagulation (under tension), C) 30 min of coagulation (no tension).